

AD-A286 562



## ENTATION PAGE Dist. A

Form Approved  
OMB No. 0704-0188

Estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Washington Headquarters Services, Directorate for Information Operations and Resources, 1215 Jefferson Dr. S.W., Washington, DC 20318.

REPORT DATE October 31, 1994 REPORT TYPE AND DATES COVERED Final 4/91-8/94

## 4. TITLE AND SUBTITLE

NOVEL REAGENTS FOR CHEMICAL VAPOR  
DEPOSITION OF INTERMETALLIC ALLOYS

## 5. FUNDING NUMBERS

2303-B2  
61102F

## 6. AUTHOR(S)

Rein U. Kirss

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Northeastern University  
360 Huntington Ave.  
Boston, MA 021158. PERFORMING ORGANIZATION  
REPORT NUMBER

AFOSR-TR- 94 0723

## 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NE NL  
Building 410, Bolling AFB  
20332-6448  
Dr. Hedberg10. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

AFOSR-91-0207

## 11. SUPPLEMENTARY NOTES

## 12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release; Distribution is unlimited

## 12b. DISTRIBUTION CODE

A

## 13. ABSTRACT (Maximum 200 words)

Reactions of  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$  with  $\text{AlMe}_3$  proceed by formation of covalently bonded heterobimetallic intermediates with no alkyl exchange. Reaction with  $\text{AlH}_3\cdot\text{NMe}_3$  yielded  $\text{Al}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{NMe}_3$  and " $\text{Hf}(\text{CH}_2\text{SiMe}_3)_3\text{H}_3$ ". Carbon blocks coated with this mixture produced a  $\text{HfAlC}_2$  coating which was effective in protecting the substrate from air oxidation at high temperatures.

DTIC QUALITY INSPECTED 5

## 14. SUBJECT TERMS

Molecular precursors, ternary metal/aluminum carbides, oxidation protection, carbon composites.

## 15. NUMBER OF PAGES

9

## 16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

U

18. SECURITY CLASSIFICATION  
OF THIS PAGE

U

19. SECURITY CLASSIFICATION  
OF ABSTRACT

U

## 20. LIMITATION OF ABSTRACT

U

## FINAL PROJECT REPORT

**TITLE:** Novel Reagents for Chemical Vapor Deposition of Intermetallic Alloys

**CONTRACT GRANT NUMBER:** AFOSR-91-0207

**SENIOR RESEARCH PERSONNEL:** Rein U. Kirss

William Feighery

Jozsef Kreisz

Lamartine Meda

**JUNIOR RESEARCH PERSONNEL:** Douglas Gordon

Northeastern University

Northeastern University

Northeastern University

Northeastern University

ATM, Inc.

ion For	
CRA&I	X
TAB	
monitored	
education	
static life	
AVL	
TA	
Dist	

A-1

**PUBLICATIONS:**

"Alkyl for Hydride Exchange Between Alane-Trimethylamine and Group IVB Metal Alkyls"

William G. Feighery, Rein U. Kirss, Charles H. Lake, and Melvyn Rowen Churchill, *Inorg. Chim. Acta*, 1994, 218, 47-51.

"Reactions of Tetrakis(trimethylsilylmethyl)hafnium With Trimethylaluminum"

Rein U. Kirss, William G. Feighery, and Douglas C. Gordon, *Inorg. Chim. Acta*, 1994, in press

**ABSTRACT:**

Alkyl exchange reactions between group IVB transition metal alkyls ( $M R_4$  where  $M = Ti, Zr, Hf$  and  $R = Me_3CCH_2, Me_3SiCH_2$ ) and aluminum alkyls ( $AlR_3$ , where  $R = Me, Et, H$ ) were studied by multinuclear NMR spectroscopy ( $^1H, ^{13}C, ^{27}Al$ ). In the case of  $Hf(CH_2SiMe_3)_4$  and  $AlMe_3$ , evidence for the formation of neutral bimetallic complexes was observed without the observation of alkyl exchange. Reactions between  $Hf(CH_2SiMe_3)_4$  and  $AlH_3 \cdot NMe_3$  yielded  $Al(CH_2SiMe_3)_3 \cdot NMe_3$  and " $HfH(CH_2SiMe_3)_3$ ". The former was characterized by single crystal x-ray diffraction. In all other exchange reactions, decomposition was too rapid for the observation of alkyl exchange or intermediates. Pyrolysis of  $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$  mixtures yielded black powders which analyzed for " $HfAlC_2$ ". Carbon blocks were dip-coated with  $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$  mixtures and pyrolyzed to give an mixed metal oxide / metal carbide coatings which gave some measure of oxidation protection at  $600^\circ C$ .

**94-35956**



119

## Introduction

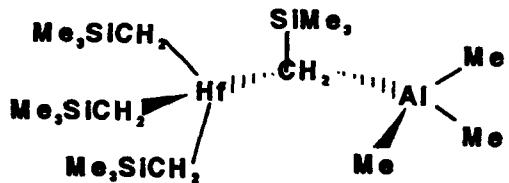
We have been investigating molecular precursors for the chemical vapor deposition of intermetallic alloys of aluminum and group IVB transition elements (Ti, Zr, and Hf) on carbon substrates as oxidation protection for the carbon materials. Our efforts have been concentrated in three areas:

1. investigations of the alkyl exchange reactions between group IVB and aluminum alkyls,
2. preparation and characterization of ternary aluminum/group IVB metal carbides from molecular precursors, and
3. evaluation of coatings prepared from molecular precursors in 2 with respect to oxidation protection of carbon blocks.

Further details of each of these projects is provided in the attached manuscripts/reprints.

## Exchange Reactions

Reactions between  $TiMe_4$ ,  $Cp_2ZrMe_2$  or  $Hf(CH_2SiMe_3)_4$  and  $AlMe_3$  were investigated using conductivity measurements and  $^1H$  NMR spectroscopy. Little change was observed in the conductivity of  $Hf(CH_2SiMe_3)_4/AlMe_3$  or  $AlMe_3/Cp_2ZrMe_2$  mixtures in dichloromethane relative to the molar conductivity of the reactants. In the presence of  $PEt_3$ , a small increase in conductivity was observed for the latter solution. A fifty fold increase in the conductivity was observed in mixtures of  $TiMe_4$  and  $AlMe_3$ . Spectroscopic studies on mixtures of  $Hf(CH_2SiMe_3)_4$  and  $AlMe_3$  were consistent with formation of a thermally unstable, alkyl bridged heterobimetallic complex, 1, present in a 5:1 ratio to the starting materials. There was no evidence for alkyl exchange in these reactions.



1

Reaction of equimolar amounts of  $AlH_3 \cdot NMe_3$  and  $M(CH_2SiMe_3)_4$  in benzene (for  $M=Zr, Hf$ ) led to exchange of all three  $Al-H$  bonds for  $Al-CH_2SiMe_3$  bonds and isolation of  $Al(CH_2SiMe_3)_3 \cdot NMe_3$  (2).

The latter compound crystallized  $P\bar{1}$  space group,  $a$  9.535(2),  $b$  10.913(2),  $c$  12.273(2) Å,  $\alpha$  88.03(1),  $\beta$  86.03(1),  $\gamma$  86.93(1)°,  $U$  1271.6(4) Å<sup>3</sup>,  $D_c$  1.002 g cm<sup>-3</sup>,  $Z$ =2,  $\mu$ (Mo-Kα) 0.217 mm<sup>-1</sup>,  $F(000)$ =424. Similar reactions between AlH<sub>3</sub>·NMe<sub>3</sub> and Cp<sub>2</sub>ZrR<sub>2</sub> (R = CH<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>) yielded Cp<sub>2</sub>ZrH<sub>2</sub> and AlR<sub>3</sub>·NMe<sub>3</sub>. Reaction of AlH<sub>3</sub>·NMe<sub>3</sub> with Zr(CH<sub>2</sub>Ph)<sub>4</sub> produced Al(CH<sub>2</sub>Ph)<sub>3</sub>·NMe<sub>3</sub>.

#### **Preparation of Ternary Group IVB Aluminum Carbides From Molecular Precursors**

Reaction of Hf(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> or Zr(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> with one equivalent of AlH<sub>3</sub>·NMe<sub>3</sub> in solution, followed by evaporation of the solvent and pyrolysis of the residue under argon (850°C for 16 hours), yielded a black crystalline powder, impervious to all mineral acids and strong oxidizing solutions. Combustion analyses for C, H and N were consistent with a formulation as HfAlC<sub>2</sub> and ZrAlC<sub>1.4</sub>. EDX analysis revealed the presence of both aluminum and hafnium in the HfAlC<sub>2</sub> product. Silicon was not detected in the latter measurements. The reaction of Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> with AlH<sub>3</sub>·NMe<sub>3</sub> at room temperature resulted in immediate decomposition without detection of any intermediates. Combustion analysis of the annealed products from reactions of Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>/AlH<sub>3</sub>·NMe<sub>3</sub> were consistent with the formulations TiAlC<sub>1.2</sub> based on retention of the initial 1:1 stoichiometry of the metals.

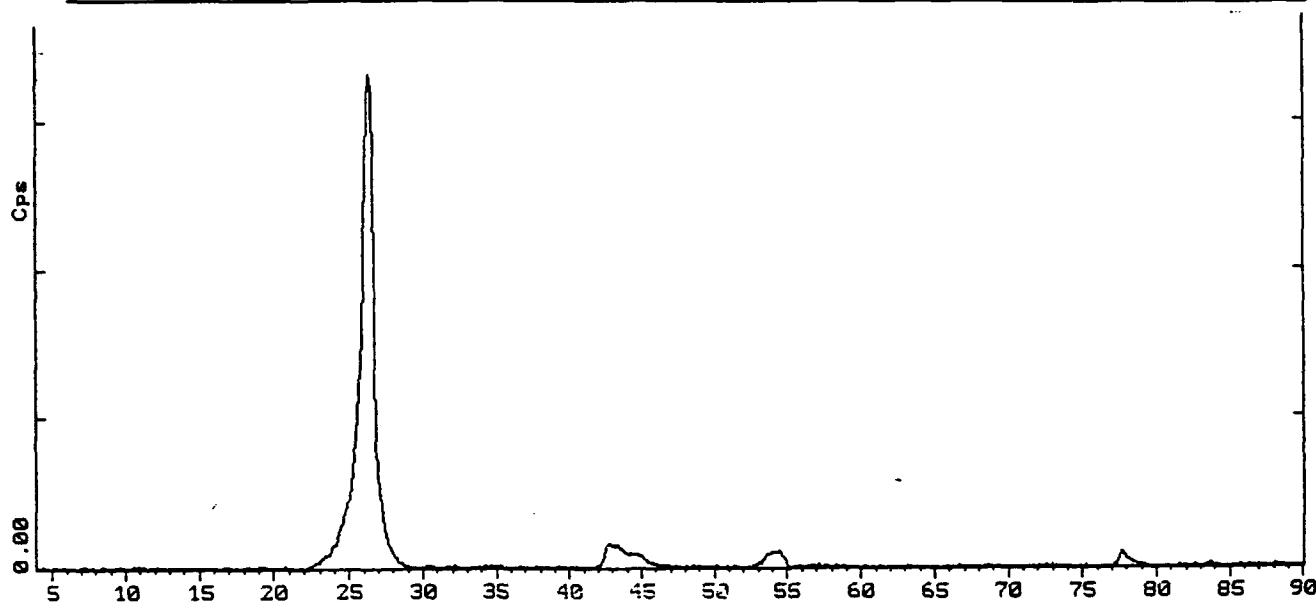
#### **Evaluation of HfAlC<sub>2</sub> Coated Carbon Blocks In An Oxidative Environment**

When solutions generated from Hf(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub> and AlH<sub>3</sub>·NMe<sub>3</sub> were used to coat carbon blocks and annealed under argon, thin coatings of the HfAlC<sub>2</sub> phase were obtained. ESCA analysis (Table 1) of the coated blocks were consistent with a 1:1:2 stoichiometry for the three elements, respectively, however, large amounts of oxygen, most likely in the form of metal oxides was also observed. The most likely source of metal oxides is believed to be the result of atmospheric oxygen introduced during the annealing process through small leaks in the system combined with high annealing temperatures and long annealing times. This conclusion is supported by the nearly constant or slightly increasing concentrations of aluminum and hafnium as a function of depth while the oxygen concentration decreases steadily when sputtered below the surface layer. The formation of metal oxides is not necessarily a major problem for coatings applications, as air oxidation of the metal carbide coating to metal

oxides is anticipated to be the mechanism for protection of the substrate. Alumina in particular has been investigated as oxidation resistant coatings for carbon based materials. Powder diffraction experiments on the coated blocks reveal a single major peak likely to correspond to diffraction by the carbon substrate. Smaller, broader peaks were too weak in intensity to identify the nature of the coating (Figure 1).

**Table 1: ESCA Analysis Of T300 Carbon Blocks Coated From  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$**

Coating Solution	Depth (Å)	$/\text{AlH}_3\cdot\text{NMe}_3$ Mixtures			
		H	Al	Atom %	
		Si	C	O	
single coat from hexane solution	surface	11.3	25.0	5.2	31.2 27.3
	20	11.9	26.3	4.7	28.1 29.0
	3000	8.8	5.8	0	72.4 13.0
triple coat from benzene solution	surface	4.4	9.2	6.4	42.5 37.5
	20	5.8	9.1	5.7	39.4 40.0
	320	6.9	6.2	3.4	58.7 24.8



**Figure 1: X-ray Powder Diffraction Pattern of T300 Block Coated With  $\text{HfAlC}_2$**

The oxidation behavior of carbon blocks coated with a single layer of mixed metal carbides from  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4 / \text{AlH}_3\cdot\text{NMe}_3$  mixtures coated blocks was evaluated by pyrolysis in air at 600°C and 900°C with the results summarized in Table 2. The data show that the  $\text{HfAlC}_2$  coating acts to protect the underlying carbon substrate for short periods, although the degree of protection from this single coating is understandably far from optimal. The 41% ceramic yield of  $\text{HfAlC}_2$  from mixtures of  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$  and  $\text{AlH}_3\cdot\text{NMe}_3$  was expected to produce cracks and pinholes in the coating exposing the underlying carbon

substrate to air oxidation. The concentration of the coating solution has a measurable effect on the oxidation behavior of the blocks. The highest concentrations appear to leave thicker coatings more susceptible to cracking as observed by SEM. Very dilute solutions provide for inadequate surface coverage, exposing the substrate to rapid air oxidation. Coatings prepared from benzene solutions of  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$  and  $\text{AlH}_3\cdot\text{NMe}_3$  were observed to be superior than coatings prepared in hexane solution.

**Table 2: Oxidation Protection of T300 Carbon Blocks By A Single Coat of  $\text{HfAlC}_2$**

Concentration of Coating Solution	% Weight Loss after 4 hours at	
	600°C	900°C
Uncoated T300	28.5	85.5
1.0 M	21.4	61.6
0.1 M	16.6	32.6
0.05 M	11.5	35.6
0.01 M	13.3	85.3

The effect of multiple coatings on the oxidation behavior of carbon blocks are summarized in Table 3. The multiple coated blocks were prepared at a constant concentration of 0.1 M for the coating solution by repetition of the coating and annealing cycles as described above for the single coated blocks.

**Table 3: Oxidation Protection of T300 Carbon Blocks By Multiple Coats Of  $\text{HfAlC}_2$**

Number of Coating Annealing Cycles	600°C/4 h	% Weight Loss 600°C/10 h	900°C
1	12.0	40.2	
2	15.9	40.7	35.6
3	16.92	29.0	

As expected, the rate of oxidation increases with temperature. The rate of oxidation (Figures 2-4) for the different number of coatings appears to be qualitatively the same for the single, double and triple coated blocks, suggesting that 1) multiple coatings are unable to fill the space left by the initial coating (i. e. pinholes, cracks are of molecular dimensions) or 2) the coating materials themselves are chemically modified and either consumed or detached from the block exposing the carbon substrate to air oxidation. Prolonged oxidation of a triple coated block at 900°C (8 hours) leads to complete consumption of the carbon block leaving a residual white crystalline powder identified by x-ray diffraction as  $\text{HfO}_2$  (Figure 5).

Data from "344-18-1"

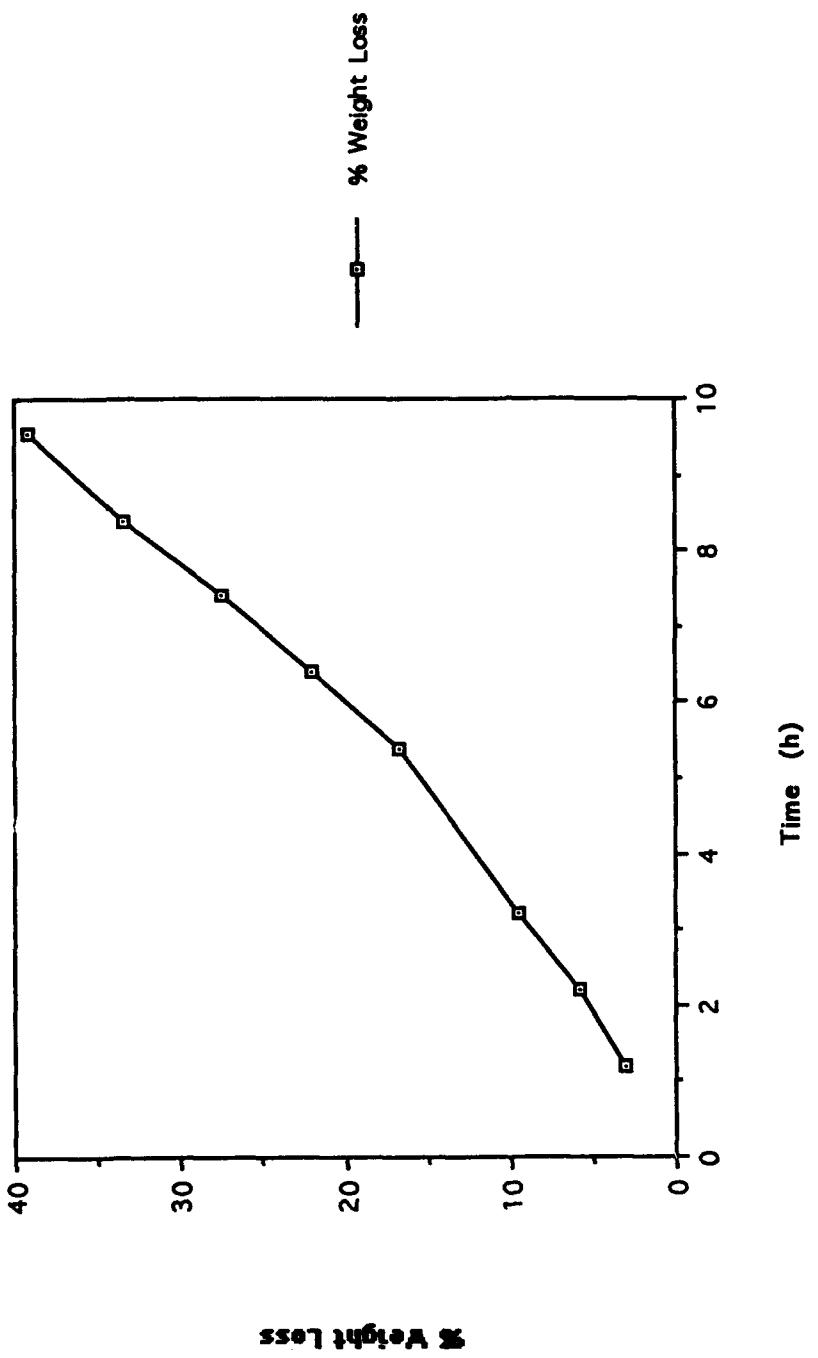


Figure 2: Oxidation Rates of Single Coated T300 Block

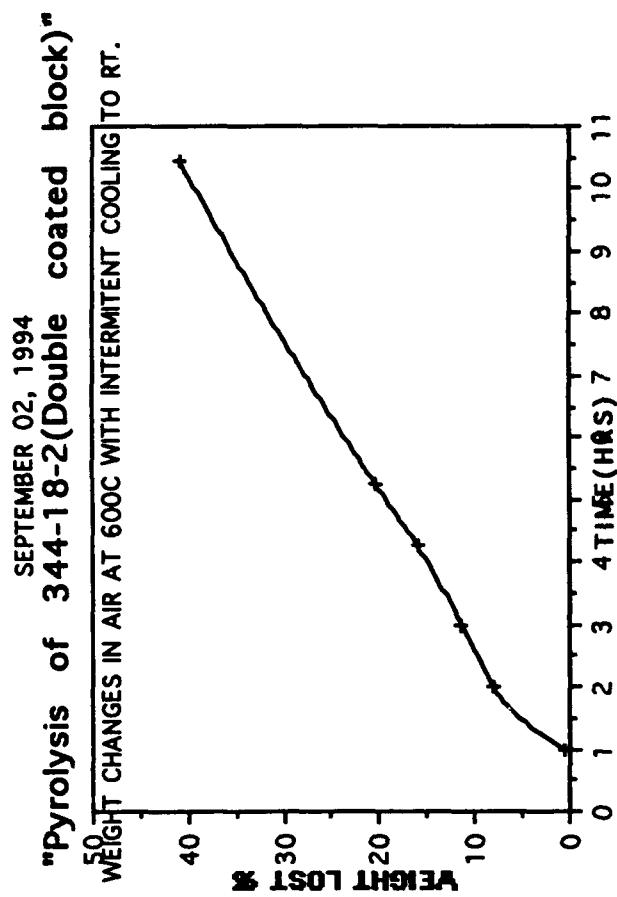


Figure 3: Oxidation Rates of Double Coated T300 Blocks

Data from "344-18-3"

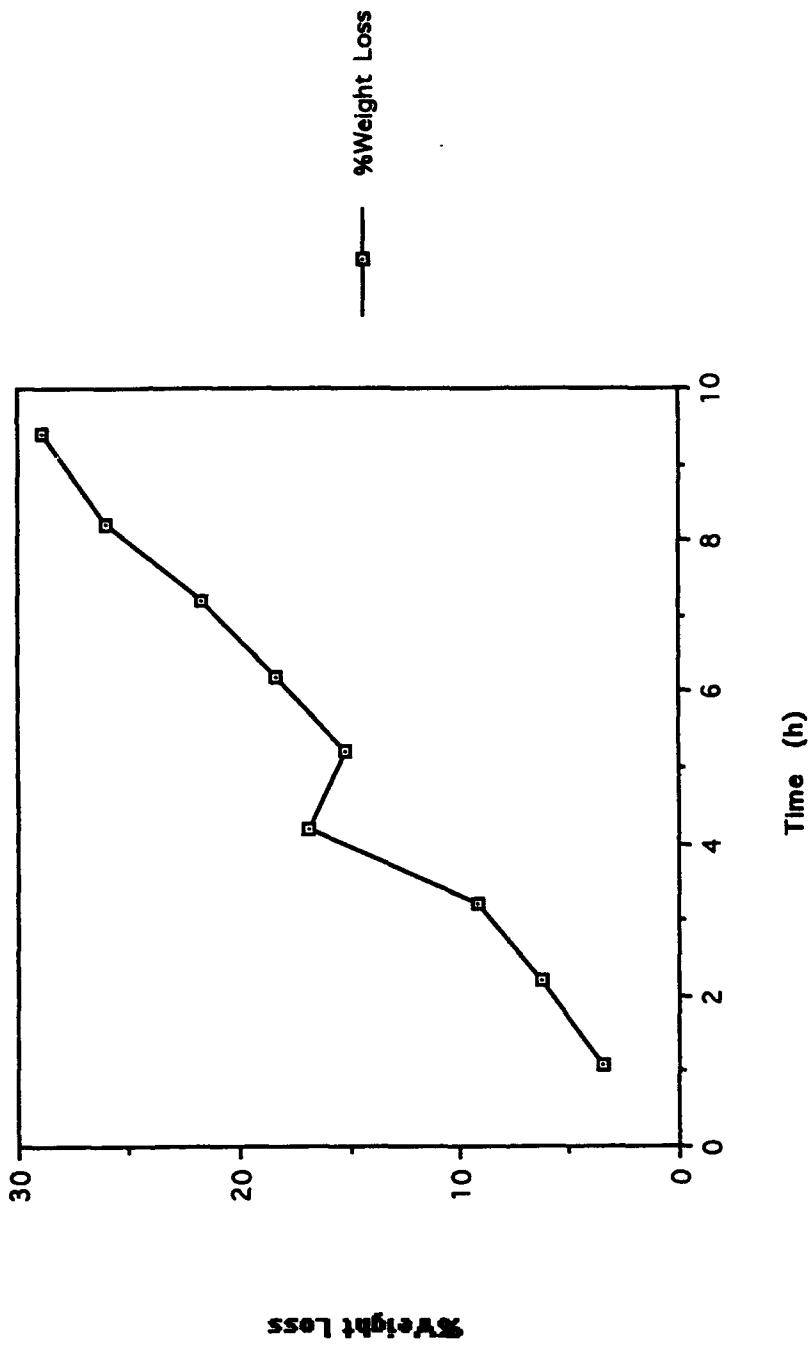
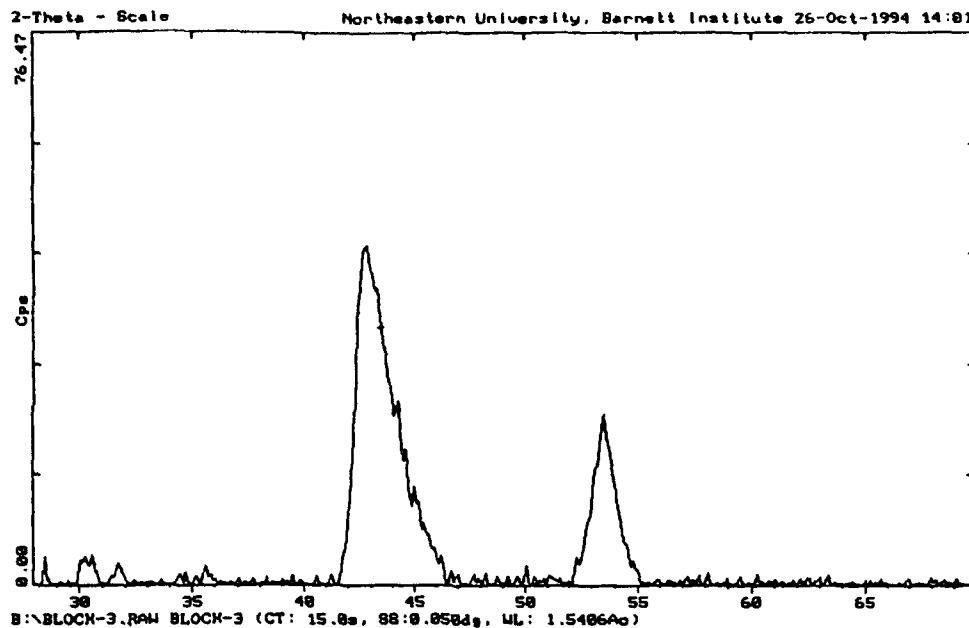


Figure 4: Oxidation Rates of Triple Coated T300 Blocks



**Figure 5: X-ray Powder Diffraction Pattern of Residue From Complete Pyrolysis Of A T300 Block Coated With "HfAlC<sub>2</sub>"**

The fate of the aluminum present initially in the coating remains undetermined, although it is possible that the diffraction pattern in Figure 5 contains a mixture of Al<sub>4</sub>C<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> (Table 4).

**Table 4: X-ray Powder Diffraction Data For Completely Oxidized T300 Blocks Coated With "HfAlC<sub>2</sub>"**

2-THETA	INTENSITY	R-INTENSITY	
28.439	4	8.69565217	HfO <sub>2</sub>
30.194	5	10.8695652	
30.632	4	8.69565217	
31.656	3	6.52173913	HfO <sub>2</sub> , Al <sub>4</sub> C <sub>3</sub>
34.435	1	2.17391304	"
34.654	1	2.17391304	"
35.532	3	6.52173913	"
42.844	46	100	C
43.283	41	89.1304348	C, Al <sub>2</sub> O <sub>3</sub>
44.234	24	52.173913	C
44.399	17	36.9565217	
44.965	12	26.0869565	HfO <sub>2</sub>
50.083	3	6.52173913	HfO <sub>2</sub>
53.52	23	50	Al <sub>2</sub> O <sub>3</sub>

## **Conclusions**

The present study on the development of novel organometallic reagents for chemical vapor deposition of early transition metal and aluminum containing materials for oxidation protection of carbon substrates leads to the following conclusions:

1. Alkyl exchange between volatile alkyl group IVB transition metals and aluminum alkyls does not occur
2. Alkyl for hydride exchange between volatile alkyl group IVB transition metals and  $\text{AlH}_3\cdot\text{NMe}_3$  is rapid
3. Pyrolysis of mixtures  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$  and  $\text{AlH}_3\cdot\text{NMe}_3$  yields ternary metal carbide products analyzing for "HfAlC<sub>2</sub>"
4. The material obtained from solution coating  $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$  and  $\text{AlH}_3\cdot\text{NMe}_3$  mixtures onto carbon blocks followed by annealing under argon provides a measure of oxidation protection for the underlying substrate for short time periods at temperatures in the vicinity of 600°C.